

Cesium, a water-incompatible, siloxane-complexed cation in Earth's upper crust

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ABSTRACT

Despite similarities in geochemical behavior, Cs and Rb concentrate in the upper continental crust (UCC) preferentially to K. Illite, a K-depleted dioctahedral mica occurring in large proportions in all types of sedimentary rocks, has high selectivity to Cs and Rb with irreversible adsorption in crystallite wedges and frayed edge sites. Analyzing 4000+ samples from 22 basins and sub-basins throughout the world using statistical computation, we found that Cs concentrates almost exclusively in illitic minerals (illite, illite-smectite) while Rb is equally distributed between K-feldspar and illite. Illite has Cs/K ratios up to 3× (median 1.97×) higher than average UCC, whereas its Rb/K variability corresponds to 1.0× to 1.08× the UCC's. Cs/Rb ratios in illite fall within the range covering average ratios for UCC, loess, and river suspension. Cs/K and Cs/Rb ratios in illite are formation specific and are higher with thinner illite crystallites, where the proportion of frayed edges to basal plane is high. With average Cs content of 17.7 ppm, illite is suggested to be a global sink for Cs on Earth's surface. Using mass balance, we present that parts-per-million concentrations of Cs adsorbed by illite crystallite edges constitute up to 20% of Cs present in UCC. Based on cation hydration enthalpy, we introduce the “water-incompatibility” concept to explain the Cs > Rb > K order of cation selectivity in illite, which is also the order of the cations' relative depletion in global seawater with respect to the UCC.

INTRODUCTION

Cesium and rubidium are large-ion-lithophile and strongly incompatible elements known to follow a general geochemical pathway of potassium. Among different zones of the lithosphere, the highest Cs/K and Cs/Rb ratios (0.16×10^{-3} and 0.04, respectively; McLennan, 2001) occur in the upper continental crust (UCC), suggesting a global-scale Cs selectivity over Rb and K, likely controlled by soils and sedimentary rocks unique to UCC (White, 2013). Indeed, soils and loess yield Cs/K and Rb/K ratios several to tens of times greater than the UCC (McLennan, 2001; Wampler et al., 2012). Illite, a potassium-depleted dioctahedral micaceous mineral, and hydroxy-interlayered dioctahedral vermiculite are common soil minerals known for high Cs and Rb selectivity (Brouwer et al., 1983; Evans et al., 1983). These two clays feature irreversible adsorption of Cs and Rb in crystallite wedges and frayed edge sites (Wampler et al., 2012; Fuller et al., 2015), which have been studied extensively for the critical role in ¹³⁷Cs retention in soil. Cs fixation on micaceous edges followed by Cs migration in the crystal structure is a suggested long-term, bio-unavailable retention mechanism (Evans et al., 1983; McKinley et al., 2004; Fuller et al., 2015). In bulk sedimentary rocks even hundreds of million years old,

batch adsorption and leaching tests found illite and illite-like mica remnants to be active components responsible for Cs fixation (Bradbury and Baeyens, 2000; Wampler et al., 2012; Chen et al., 2014). Although weathered phlogopite, biotite, and trioctahedral vermiculite were found to be the primary soil components responsible for radiocesium fixation (McKinley et al., 2004; Mukai et al., 2016), these minerals are highly susceptible to chemical weathering and rarely survive long transport; only their dioctahedral, Al-rich derivatives reach sedimentary basins (Wilson, 2004).

The log selectivity coefficients of Cs, Rb, and K with Na in illite reach 7, 4–5, and 2.2–2.4, respectively (Bradbury and Baeyens, 2000), making illite the best common sedimentary mineral to bind soluble Cs at the basin scale. Illite may play a key role in differentiating the geochemical pathways of K, Cs, and Rb in sedimentary rocks wherever the fractionation occurs. In this study we determined the distribution of Cs and Rb among sedimentary rock minerals to find the Cs/K and Rb/K ratios in illite from different sedimentary basins, and to evaluate the illite contribution to Cs enrichment in the UCC.

SAMPLES AND METHODS

The mineral and elemental compositions were analyzed for >4000 bulk samples collected from 110 wells drilled in 22 basins throughout

the world in strata of lower Cambrian to Pliocene age and with varying thermal maturation and burial history (Fig. 1; Tables DR1 and DR2 in the GSA Data Repository¹). Carbonate systems, numerous shale and black shale formations, shallow opal-rich heavy oil reservoirs, and deep-water and terrigenous deposits are represented. All 2:1 layer dioctahedral clay and mica minerals potentially contributing to Cs and Rb fixation were quantified together as an illite + smectite mineral group in the applied mineral quantification method employing custom-protocol X-ray diffractometry (Środoń, 2009; McCarty et al., 2015). The illite + smectite mineral group is hereafter called illite because this mineral group is dominated by interstratified illite-smectite with a mostly illitic character in most studied sections (cf. Środoń, 2009; McCarty et al., 2015; see supplemental methods in the Data Repository). The contribution of a given mineral to the bulk rock concentration of a given element was estimated by assuming the element's constant concentration in the mineral throughout the entire section. The calculation was considered valid when the multivariable equations for a sample set returned a good match between the measured and calculated bulk-rock concentrations based on individual mineral content and its optimized elemental formula (McCarty et al., 2015; see the Data Repository). Each of 110 data sets (sections, basins), containing from eight to 165 samples, represents a different calculation model resulting in an optimized Rb, Cs, and K concentration in the mineral phase.

Using conventional chemical and mechanical separation procedures, mineral fractions <1.0 and <0.5 μm were extracted from samples collected across a bentonite (altered ash) bed from the Montana (USA) disturbed belt (Cretaceous Marias River Shale). Besides detailed chemical and mineralogical studies (data from McCarty et al., 2009), the clay fractions were dated using the ⁴⁰Ar-³⁹Ar “total gas” method customized for illite (Dong et al., 1997; see the Data Repository methods).

¹GSA Data Repository item 2017294, Tables DR1 and DR2, and materials and methods, is available online at www.geosociety.org/pubs/ft2017.htm or on request from editing@geosociety.org.

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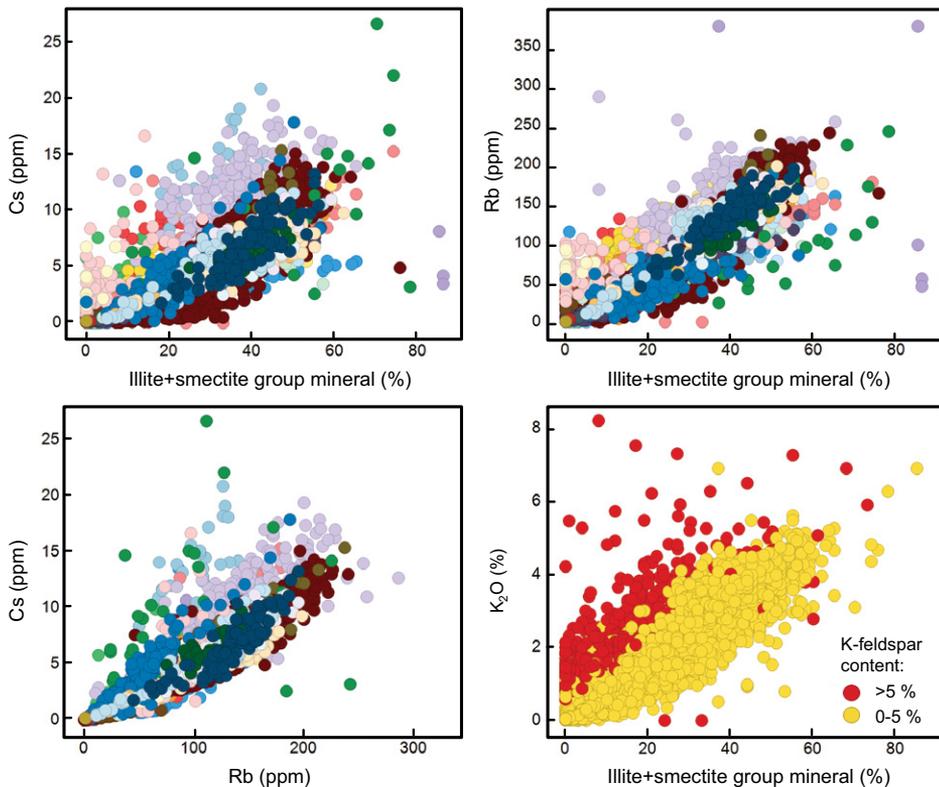


Figure 1. Relationships between Cs, Rb, and K_2O concentrations and total illite + smectite group mineral content in bulk samples from studied formations (Table DR1 [see footnote 1]). Except color-coding for K-feldspar content, colors indicate different sections studied.

RESULTS

Sedimentary Basins

Illite and K-feldspar are the most common K-bearing minerals in sedimentary rocks. K-feldspar and mica are detrital components transported to sedimentary basins from the older, weathered rocks of any origin (Wilson, 2004). During burial, decomposing K-feldspar is a major source of K for illitization (Wilkinson et al., 2001). The initial statistical analysis revealed, with few exceptions, that illite and K-feldspar are the only K-, Rb-, and Cs-bearing minerals (Fig. 1) in the sections studied, and thus these elemental concentrations were distributed between K-feldspar and illite. The 83 statistically valid models of Cs, Rb, and K distribution in illite revealed median Cs and Rb contents of 17.7 ($1\sigma = 5.2$) and 315 (± 79) ppm, respectively (Table DR2). The calculated median K content in illite is $6.1\% \pm 1.4\%$ and closely matches the theoretical values for illite-rich interstratified illite-smectite minerals (Środoń, 2009; McCarty et al., 2009). Only 35% of the studied sections contain K-feldspar in a quantity and variability to allow considering K-feldspar in the Rb and Cs statistical distribution (see the Data Repository for details). In those 36 models, Rb concentration in K-feldspar was highly variable with a median of 234 ± 156 ppm and almost always lower than in the corresponding illite from the same section. Half of the valid models, however,

returned an absence of Cs in K-feldspar, and only four models showed Cs > 10 ppm, which is reflected in the average 2.0 ± 3.1 ppm.

The Cs/K and Cs/Rb ratios in illite seem to be formation specific (Fig. 2; Table DR2). A mean UCC-normalized Cs/K (Cs/K_{UCC}) of 1.47 ± 0.10 was found in the Silurian shale in the Baltic Basin (northern Poland, Lithuania) and the Lublin Basin (southeast Poland). An illite Cs/K_{UCC} of 2.16 ± 0.10 occurs in the Permian Wolfcamp Formation across the Delaware Basin (Texas and New Mexico, USA) whereas the

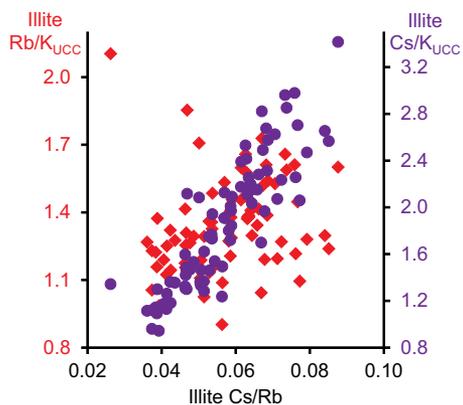


Figure 2. Relationships between Cs/Rb and upper continental crust (UCC)-normalized Cs/K and Rb/K (Cs/K_{UCC} , Rb/K_{UCC}) ratios calculated for illite from sedimentary basins, based on 83 statistically valid models.

ratio is slightly lower in the neighboring Midland Basin. Illite Cs/K_{UCC} and Cs/Rb ratios similar to those of the Wolfcamp Formation were obtained for the Jurassic Haynesville Formation in east Texas. In Western Australia's Triassic Mungaroo Formation in the Exmouth Plateau, Cs/K_{UCC} and Cs/Rb vary significantly from 0.96 to 2.28 and from 0.026 to 0.066, respectively, allowing for distinct discrimination among gas fields developed over the large geographic area of the Western Australia shelf. The highest Cs/Rb and Cs/K_{UCC} values were found in illite from the Whitehill Formation of the Karoo Supergroup in South Africa, 0.071 ± 0.005 and 2.77 ± 0.19 , respectively, which are similar to those in the Vaca Muerta Formation of Argentina and the Miocene-age Surma Basin in Bangladesh. Similarly high Cs/Rb and Cs/K_{UCC} ratios perfectly discriminate the Muskwa Formation from its equivalent in central Alberta in Canada (Duvernay Formation: 0.051 ± 0.004 and 1.34 ± 0.08 , respectively). Illite in the deep-water Gulf of Mexico mudstones and sandstones cluster at a Cs/Rb ratio of 0.068 ± 0.007 . The most spectacular example comes from the Utica and overlaying Marcellus Formations in Pennsylvania and Ohio (USA) whose Cs/K_{UCC} and Cs/Rb ratios are distinctively different even in the same wellbore (e.g., 1.14 versus 1.75 for Cs/K_{UCC} and 0.038 versus 0.053 for Cs/Rb). Within the Marcellus Formation, however, the values clearly increase with thermal maturation (Cs/K_{UCC} from 1.72 to 2.31 and Cs/Rb from 0.053 to 0.068; Fig. 3).

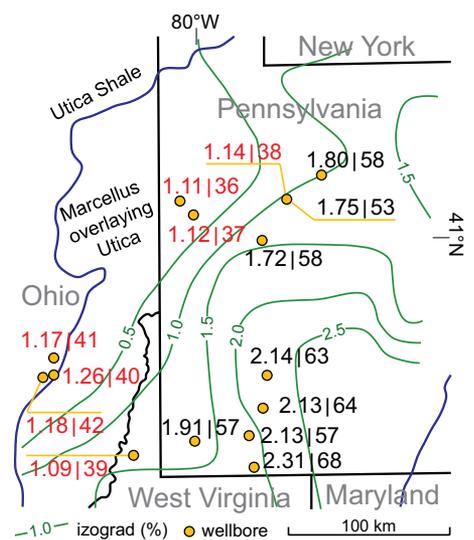


Figure 3. Map covering Devonian Marcellus Formation and Ordovician Utica Formation in Pennsylvania and Ohio (USA) with Devonian isograds of vitrinite reflectance (green, in %; Ryder et al., 2013). Thick blue lines bracket the area where Marcellus Formation overlies Utica Shale. Values of Cs/Rb (in 10^3 units) and upper continental crust (UCC)-normalized Cs/K_{UCC} ratios calculated for illite from Utica Shale (red) and Marcellus Formation (black) are shown in format of " Cs/K_{UCC} | Cs/Rb ".

Bentonite's "Natural Laboratory"

Smectite forms in a nascent volcanic ash as the first alteration product of glass. In the studied bentonite from Montana (USA), the progress of diagenetic illitization of smectite was limited by the rate of K migration from the sandwiching black shale formations toward the center of the bentonite bed (Fig. 4) (McCarty et al., 2009). The resulting decrease of the illitic component's fraction in the interstratified illite-smectite structure correlates with decreasing illite Ar-Ar age (cf. Altaner et al., 1984). The Cs/K and Rb/K ratios in the fine-fraction illite-smectite clearly increase with the degree of smectite illitization and thus K content in the crystallites (Fig. 4). The measured illite Rb/K ratio in the bentonite covers the variability found in illite from shales (cf. Fig. 2), whereas illite Cs/K ratios are much greater than found in shales, reaching Cs/K_{UCC} of 8.5 at the upper contact. The illite K contents and Rb/K ratios overlap in the two grain-size fractions. The calculated rate of Rb fixation is roughly 25% faster than that of K fixation, making the Rb/K also increase with illitization. In turn, Cs/Rb is invariant of Ar-Ar age, illitization, and K content within the central part of bentonite. Cs/K and Cs/Rb ratios are much greater in the finer fraction, where they reach values 50%–100% higher than those calculated for illite in sedimentary basins, whereas the Cs/K in the coarser fraction is close to the maximum of illite in shales (cf. Fig. 2). Such relationships imply that, whereas Rb follows illitization with preferential fixing over K, Cs content depends mostly on the illite crystallite size.

DISCUSSION

In all of the statistically significant models, illite has Cs/K ratios up to 3× (median 1.97×) higher than in the UCC. Rb/K_{UCC} variability in illite is much lower (1.0× to 1.08×), with few exceptions. In K-feldspar, median Rb/K is roughly half of that in the UCC, whereas the Cs/K_{UCC} ratio rarely exceeds 0.2 whenever Cs is present. The variability of Rb concentration closely follows that of K albeit enrichment

occurs in illite. The modeled Cs/K_{UCC} and Rb/K_{UCC} in illite seem to correlate positively, but Cs/Rb also increases along with Cs/K (Fig. 2). The majority of calculated Cs/Rb ratios in illite fall within the range covering an average ratio for the UCC (0.041), average loess (0.052), and average river suspension (0.078; McLennan, 2001). Thus, the Cs segregation with respect to both K and Rb in sedimentary basins is strongly controlled by illite and K-feldspar.

The finer the illite size fraction, the greater the proportion of illite crystallite edges to the planar dimension, and thus more potentially exposed frayed edges. The observed increase of Cs/Rb and Cs/K_{UCC} with increasing thermal maturation in the Marcellus Formation (Fig. 3) must thus be associated with nucleation and growth of new illite particles, which is precisely how the illite nucleation progresses in the studied bentonite bed from Montana (cf. Fig. 4; Śródoń et al., 2002; McCarty et al., 2009). The same mechanism related to a crystallite aspect ratio produces low Cs/K ratio in macroscopic-size muscovite (except those from rare Cs-rich pegmatite) in contrast to maximum Cs/K reached in soil dioctahedral vermiculite, which is essentially a frayed-edge equivalent in an entire crystallite (Wampler et al., 2012). Although smectite, a common illite precursor, has a high cation-exchange capacity, its surface is not selective to Cs or Rb fixation (e.g., Chen et al., 2014). Following the adsorption mechanism for other alkaline and alkaline-earth cations on smectite, Cs and Rb complexed in an outer-sphere position can desorb immediately, unless inner-sphere fixing in the ditrigonal cavity occurs (Evans et al., 1983; Sato et al., 2016). If adsorbed on illite frayed edges or in a vermiculite interlayer, Cs is fixed irreversibly by bonding directly to two adjacent siloxane surfaces of tetrahedral sheets near the site of Al³⁺ for Si⁴⁺ substitution (Bostick et al., 2002; Chen et al., 2014; Fuller et al., 2015; Gimmi and Kosakowski, 2011; Wampler et al., 2012). Therefore, smectite particles in the Montana bentonite center do not have elevated Cs concentrations (Fig. 4) whereas extensive Cs

and Rb fixation occurs in the illitic environment of the bentonite's boundaries near shale.

Soil and river suspensions have Cs/K ratios several times greater than that of average UCC, and the highly water-soluble Cs⁺ (more soluble than K⁺ and Rb⁺) might be expected to transfer from a soil to a sedimentary basin via dissolution in seawater. Despite its high solubility, however, the majority of Cs is transported to sedimentary basins bound by frayed-edge and wedge sites of soil micaceous minerals (Wampler et al., 2012; Mukai et al., 2016). Although during clay alteration and illitization under diagenetic conditions Cs can be locally remobilized, it immediately enters the edge sites in newly formed illite crystallites. Cs remobilization is restricted not only by rock permeability, but mostly by immediate re-fixing in illite (Fig. 4). Therefore, adjacent sediments and formations (Fig. 4) do not exchange this highly water-soluble cation easily via free pore water, which is confirmed by low Cs mobility in soils and sedimentary rocks (Gimmi and Kosakowski, 2011; Chen et al., 2014).

The uppermost Cs contents determined in illite from sedimentary basins in the present study closely match the maximum irreversible Cs retention of 0.2 mmol/kg (= 27 ppm Cs) found in illite frayed edges using batch experiments (Poinssot et al., 1999; Bradbury and Baeyens, 2000), implying a common mechanism of Cs retention in both cases. The mean seawater Cs/K ratio is >200× lower than in the UCC, suggesting the presence of a mechanism responsible for strong depletion of Cs in seawater with respect to other alkaline cations. As deduced from the difference in Cs concentrations in shale (even triple the UCC's) in this study, seawater (0.3 ppb), and the UCC (4600 ppb), as well as the Cs adsorption experiments (Bradbury and Baeyens, 2000; Chen et al., 2014), we suggest that illite-rich marine shale is the primary sink for seawater Cs (cf. McLennan, 2001). Indeed, UCC-seawater partition coefficients of Cs, Rb, and K to hydrophilic Na (calculated based on McLennan [2001] and White [2013]) follow precisely their order of selectivity coefficients to Na in illite (Bradbury

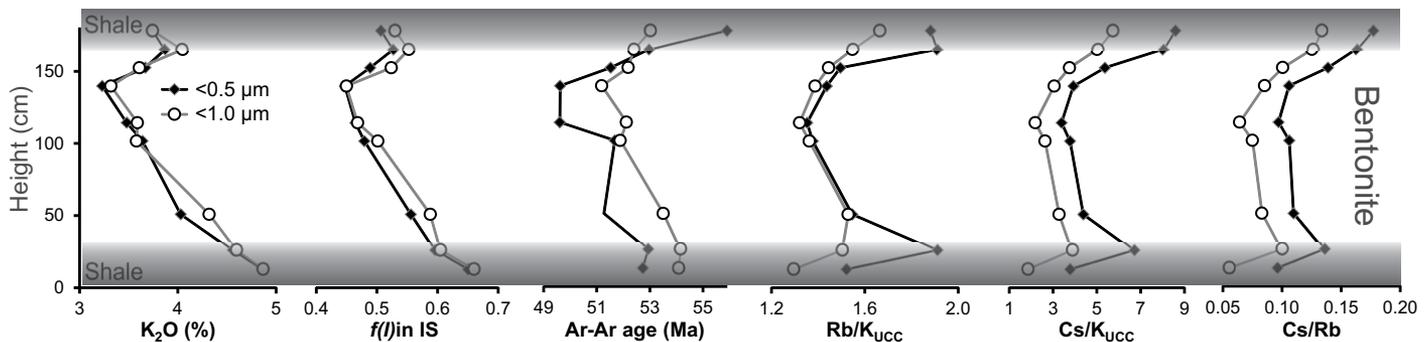


Figure 4. Data from cross section of bentonite bed from Montana (USA) disturbed belt collected on separated clay fractions <0.5 μm and <1.0 μm dominated by interstratified illite-smectite (IS). Data of K₂O content and the fraction of illite layers in IS, *f(I)*, that corresponds to the progress of illitization are from McCarty et al. (2009). Gray shows shale admixture. "UCC" subscript indicates ratios normalized to upper continental crust.

and Baeyens, 2000). To match the average 17.7 ppm of Cs concentration in illite found in this study, as little as several centimeters of illite-rich sediment covering the seafloor or <15 g of illite suspension in 1 m³ of seawater would suffice to irreversibly adsorb all Cs present in the oceans. As the Cs equilibration with frayed-edge sites of illite or inner-sphere fixing in vermiculite is complete within hours (Poinssot et al., 1999), any Cs⁺ contact with illitic material may result in its immediate fixation. We suggest that the Cs concentration observed in seawater results primarily from its equilibrium with illitic particles present in suspension or in bottom sediment (cf. Bradbury and Baeyens, 2000). Thus, Cs can justifiably be called an “illitophilic”, siloxane-complexed element.

CONCLUSIONS AND IMPLICATIONS

The Cs > Rb > K selectivity order in sedimentary illite (Brouwer et al., 1983; Bradbury and Baeyens, 2000) was confirmed by this study on global spatial and geologic time scales. The selectivity order of alkaline cations also represents the order of cation radius and inverse hydration enthalpy, which is the preference to remain complexed by H₂O rather than form an inner-sphere complex on a charged clay surface (Rotenberg et al., 2009). From a geochemical perspective, Cs⁺ is water soluble, albeit it seems to be a *water-incompatible* (an expression suggested following *incompatible elements* in petrology) cation, and the adsorption selectivity order on illite of Cs > Rb > K > Na is the order of *water incompatibility*.

Clay mineral surfaces are the most reactive mineral surfaces in the geosphere and are the almost exclusive contributor to bulk-rock specific surface area (Środoń, 2009). Illite and illite-smectite are the major clay minerals in shale, making up on average 40%, whereas they form 10% of other sedimentary rocks (Środoń, 2009). Shales make up as much as 70% of Earth's sedimentary record (Garrels and Mackenzie, 1971). With a realistic estimation that illitic minerals account for ~30% of sedimentary cover (Garrels and Mackenzie, 1971) and that sedimentary rocks form 11%–14% of the UCC (Wedepohl, 1995; White, 2013), illite is responsible for up to 20% of Cs in the UCC and is the major, or even the only, sink for Cs in global ocean and sedimentary basins. We believe that it is the Cs > Rb > K > Na *water incompatibility* order that drives the Cs enrichment in illite, which is the controlling factor of Cs and Rb pathway segregation in the UCC.

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